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AMBIENT AIR AUDITS OF ANALYTICAL PROFICIENCY
-1988-

by

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ABSTRACT

This report presents the results of the U.S. Environmental Protection Agency's 1988 National Ambient Air Performance Audit Program. Semiannual audits were conducted for lead, nitrate and sulfate on filter strips, and acid rain. One audit was conducted for high volume/PM-10 size selective inlet (SSI) sampler flow rate and carbon monoxide. Continuous sulfur dioxide monitors were audited throughout the year. Pilot-scale audits conducted for dichot sampler flow, continuous nitrogen dioxide monitors, and ozone monitors in 1988 were successful. These audits were initiated on a full-scale basis in 1989. The results for each 1988 audit (with the exception of acid rain) are presented in tabular form for each concentration level. The overall performance for all participants for each audit conducted since the beginning of the program [with the exception of sulfur dioxide and high volume/PM-10 (SSI)] is also shown graphically.

CONTENTS

	Page
Abstract	iii
Tables	v
Figures	vi
Acknowledgments	vii
1. Introduction	1
2. Results and Discussion	4
References	7
Tables	8
Figures	13

TABLES

Number		Page
1	Percent of Audit Results Within 1, 3, 5, 10, 15, and 20 Percent of the Assigned Value	8
2	Audit Results for Carbon Monoxide	9
3	Audit Results for Sulfate on Filter Strips	9
4	Audit Results for Nitrate on Filter Strips	10
5	Audit Results for Lead on Filter Strips	11
6	Audit Results for Sulfur Dioxide Continuous Monitors	12
7	Audit Results for High Volume/PM-10 (SSI) Flow Measurements	12

FIGURES

Number		Page
1	Carbon Monoxide Audits	13
2	Sulfate Audits	14
3	Nitrate Audits	15
4	Lead Audits	16

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SECTION 1

INTRODUCTION

The National Performance Audit Program (NPAP) for ambient air is conducted annually by the Atmospheric Research and Exposure Assessment Laboratory (AREAL) of the U.S. Environmental Protection Agency (EPA) at Research Triangle Park, NC. NPAP provides EPA management a means to assess the compliance of agencies that are operating monitors in the State and Local Air Monitoring System (SLAMS) network with one aspect of the minimum quality control (QC) program required under Section 2.0 of 40 CFR Part 58, Appendix A. The NPAP complements the biannual systems audits conducted on the SLAMS network by the EPA regional offices. Organizations operating SLAMS samplers and prevention of significant deterioration (PSD) site samplers are required by 40 CFR Part 58 to participate in the appropriate NPAP audits.

Although participation is mandatory for SLAMS and PSD site operators, participants can benefit from the NPAP because it provides them a means to compare their performance to that achieved by other organizations who participate. Participation in the NPAP can also identify out-of-control situations in the participant's QC program. However, an organization cannot validly use NPAP data to adjust or invalidate monitoring data unless there is a basis for doing so from its internal QC program.

Until the 1987 audits, potential NPAP participants were primarily identified by using input from the EPA regional offices and the previous year's mailing lists. This system was only moderately effective in assuring that organizations operating SLAMS and PSD sites participated in the NPAP as required under 40 CFR Part 58. Significant improvements were made in this area in 1987 as a result of changes in the SLAMS regulations to require each agency to report its precision and accuracy data from each monitor. Additional improvements were made in the 1988 audits, and by 1989 we should be able to identify and contact all organizations that must participate in the NPAP.

In 1988, audits were done on the following criteria air pollutants: sulfur dioxide, carbon monoxide, high volume/PM-10 (SSI) (flow only), and lead (analysis only). Pilot studies were also conducted in 1988 for auditing nitrogen dioxide continuous monitors (8 monitors), PM-10 dichot samplers (10 samplers), and ozone monitors (4 monitors). The pilot studies were successful and these will be full-scale audits in 1989. The addition of nitrogen dioxide, dichot sampler (flow only), and ozone audits will permit EPA to audit all the criteria air pollutant measurements under NPAP. Audits for sulfate and nitrate on filter strips and for acid rain are also done under the NPAP program. Because these are not SLAMS pollutants, participation is voluntary. These latter non-criteria pollutant audits, which check only

the analytical portion of the method, are open to governmental, academic, and commercial organizations. (Participation in most of the criteria pollutant audits is restricted to SLAMS and PSD site operators.)

In 1989, many changes were made in the NPAP. The lead audit is being conducted quarterly instead of semiannually, and two filter strips instead of three are being used. Each agency now has the opportunity to participate in the lead audit four times per year. The high volume/PM-10 (SSI) flow audit is now being conducted quarterly instead of annually which allows agencies to receive the audit device twice each year. Three new audits were added to the NPAP in 1989. Ozone and nitrogen dioxide continuous audits are being conducted on an annual basis, and the PM-10 dichot flow audit is being conducted quarterly. A letter that describes the EPA criteria for acceptable audit performance now accompanies the audit result report form sent to the participant. In addition, organizations whose performance falls outside of these performance criteria are contacted by EPA to determine the cause of poor performance and to ascertain if corrective action has been taken.

Approximately 368 organizations registered for the NPAP in 1988; 295 agencies returned results. The total number of participants has remained essentially unchanged since 1984 for all the audits concerned with criteria pollutants and for the sulfate and nitrate audits. Approximately 80 percent of these 295 organizations were governmental with the remainder primarily industrial and contractor organizations.

Our goal in 1989 is to provide participants an evaluation of their performance within one week after the audit is completed. When practical, those submitting abnormally high or low results are offered an opportunity to analyze another set of samples. However, the retest results are not included in this summary report. In any case, participants with excessively deviant values can investigate their operations to identify and correct the cause of the large errors.

Throughout this report, reference is made to "assigned values." These values are the standards against which reported results are evaluated and have been so designated after consideration of the analytical results of the referee laboratory, the Quality Assurance Division (QAD)/AREAL Standards Laboratory, and the manufacturer of the audit material. For acceptable performance, audit participants must obtain results within $\pm$ 15 percent of the assigned value except for the CO audit where the value is $\pm$ 10 percent. These performance criteria are based on the historical performance for these or similar audits. Almost all participants who follow the instructions achieve results within the $\pm$ 15 percent acceptance range.

The audit materials used in the NPAP in 1988 (with the exception of acid rain) are described below. Acid rain will be discussed in a separate report.

CARBON MONOXIDE AUDIT

These audit materials consist of a mixture of carbon monoxide, carbon dioxide, methane and zero air in a disposable pressurized gas cylinder that

simulates an ambient air sample. Directions specify that the gas sample be introduced into a continuous analyzer in the "sample" mode to permit the analyzer to draw the sample in the same fashion and at the same flow rate as during ambient air monitoring.

SULFATE, NITRATE, AND LEAD AUDITS

The filter strip samples used are 1.9 cm wide by 20 cm long. They are cut from 20- by 25-cm glass fiber filters, spiked with an aqueous solution of the appropriate solution, and oven dried. After analysis, pollution concentrations are computed by assuming that the samples were collected on the prescribed high volume filter with a sample air volume of 2000 m^3. Three sample strips comprise a set. The sulfate, nitrate, and lead samples were prepared from aqueous solutions of sodium sulfate, potassium nitrate, and lead nitrate, respectively.

SULFUR DIOXIDE CONTINUOUS MONITOR AUDIT

The auditing device for the sulfur dioxide continuous ambient air monitors is a dilution system that provides a mechanism to control the quantity of sulfur dioxide and diluent air that are mixed and then passed into the monitor. The flow rate of each gas is controlled by maintaining a predetermined pressure drop across a porous plug flow restrictor, and the sulfur dioxide concentration is changed by using different combinations of these flow restrictors.

The audit device, which is housed in a compact, lightweight, impact-resistant case, is constructed so that only the controls needed to operate the system are exposed. By opening and closing different toggle valves, it is possible to generate up to seven preset pollutant concentrations. Three are used for the audit. A compressed gas cylinder containing sulfur dioxide in nitrogen is supplied with each unit, along with a pump-based zero air system which serves as the dilution air source. Each audit device is calibrated at the three settings used in the audit with the flow calibration referenced to laminar flow elements traceable to flow standards of the National Institute of Standards and Technology (NIST), formerly the National Bureau of Standards.

HIGH VOLUME/PM-10 (SSI) FLOW AUDIT

The reference flow (ReF) device used for this audit consists of a modified orifice, a wind deflector, a manometer, and five resistance plates. A single ReF device is supplied to each participating agency with instructions to check samplers at as many sampling sites as feasible. Before use in the audit, each ReF device is calibrated with a positive displacement meter traceable to the NIST. During the audit, the device is mounted on top of the sampler and replaces the filter faceplate. The wind deflector is then positioned to prevent fluctuations in the measurements due to wind blowing across the orifice.

SECTION 2

RESULTS AND DISCUSSION

The NPAP results do not warrant a sophisticated statistical analysis for a variety of reasons. For one thing, the summary statistics cannot be used to adjust the SLAMS data base. Also, an individual audit result cannot be used by itself to invalidate data from a SLAMS or PSD monitor, and, at this time, it is not possible to compare the precision and accuracy data reported for a SLAMS monitor to that obtained in the NPAP. However, the NPAP data does provide a means to detect any general trends in the performance of organizations measuring criteria air pollutants. It also provides each participant an opportunity to compare his result to the results reported from all organizations that participated in the audit. The summary statistics and the figures in this report are adequate for these two latter purposes.

All results for the 1988 NPAP audits are summarized in tabular form by using (1) the mean and (2) the percent difference (% Diff.) of this mean from the assigned (true) value. The mean is the average of all the values reported for that concentration level. The data is presented with and without the outliers removed. Values greater in magnitude than $\pm$ 30 percent of the assigned value were deleted as outliers. The excluded values represented approximately 5 percent of the total number of results, which is approximately the same as for 1983 through 1987 (1-5). After outliers were eliminated, the results from all participants were normally distributed.

At each audit level, the percent difference was calculated by using Equation 1. The percent difference measures how well the average of all participants agrees with the assigned value.

$$\% \text{ Diff.} = \frac{\text{audit mean} - \text{EPA assigned value}}{\text{EPA assigned value}} \times 100 \qquad (1)$$

The results are also presented in terms of the percentage of the participants who reported results within 1, 3, 5, 10, 15, and 20 percent of the assigned (true) value (Table 1). These results, which are for all data, are presented as a function of each concentration or flow rate used in the audit. If two audits were done in 1988, the results from the two audits were averaged. This was done because the results from the same type of audit were very similar, particularly for the results between 5 and 20 percent of the assigned value.

Inspection of Table 1 shows that for the 1988 carbon monoxide audit, 48 percent of the participants reported a value for the Level 1 sample

that was within 3 percent of the assigned value. This table also shows that 94 percent of the participants reported a value for the Level 1 sample that was within 10 percent of the assigned value.

An overall % Diff. for carbon monoxide, sulfate, nitrate, and lead was also calculated and plotted (Figures 1 through 4) to show the historical record of performance for these audits. All of the figures present the results of the performance audits after elimination of the outliers for the years 1981 to 1988. Because of software limitations in previous years, graphs could not be generated for sulfur dioxide and high volume/PM-10 (SSI) flow.

Carbon Monoxide Audit. The number of organizations participating in this audit increased approximately 25 percent from 1986 to 1987, and remained unchanged from 1987 to 1988. The % Diff. has not changed since 1981 (Table 2, Figure 1), and the percent frequency distribution has been constant since 1983. For example, in 1988, 98 percent of the results for the Level 2 sample were within 10 percent of the assigned value. From 1983 to 1987, values for this sample ranged from 95 percent to 99 percent.

Sulfate Audit. In 1986, the number of organizations participating dropped approximately 15 percent from the 1983 to 1985 audits, and it then was constant from 1986 to 1987. Participation dropped again in 1988 by almost 22 percent. The overall results have been essentially constant for % Diff. since 1983 (Table 3, Figure 2). The percent frequency distribution has improved dramatically since 1986. For example, in 1986, 56 percent of the results for the Level 2 sample (after averaging both audits) were within 10 percent of the assigned value. This increased to 67 percent in 1987 and 88 percent in 1988.

Nitrate Audit. Like the sulfate audit, participation dropped almost 22 percent in 1988. Since 1984, the % Diff. has been reasonably constant (Table 4, Figure 3) and so has the percent frequency distribution. From 1984 to 1988, 79 to 83 percent of the results for the Level 3 sample were within 10 percent of the assigned value.

Lead Audit. In 1988, the number of organizations participating declined almost 11 percent from 1987 and 1986. The % Diff. (Table 5 and Figure 4) has remained essentially unchanged since 1981. The percent frequency distribution has also remained constant. For example, from 1986 to 1988, almost 90 percent of the results for the Level 3 sample were within 10 percent of the assigned value.

Sulfur Dioxide Continuous Monitor Audit. The number of monitors audited in 1988 (247) represents a 6 percent decrease from 1987 when 262 monitors were audited. In 1988 and 1987, 95 percent of the monitors audited used fluorescence as their measurement principle. For the first time, new software enabled calculation of the % Diff. (Table 6) and the percent frequency distribution for the 1988 audit.

High Volume/PM-10 (SSI) Flow Audit. Approximately 1118 samplers were audited, and almost 6 percent of the results were discarded as outliers. Because each NPAP audit device has unique calibration factors, only the

approximate flow (in m^3/min) can be provided for each resistance plate. New software in 1988 enabled calculation of the % Diff. for this audit for the first time (Table 7). The percent frequency distribution has declined slightly over the past three years for results within 10 percent of the assigned value. For example, results for Plate 18 have dropped from 91 percent in 1986 to 86 percent in 1988. During 1988, mass flow controlled high volume samplers came into widespread use. Eighty-four percent of these samplers (Plate 88) were within 10 percent of the assigned value.

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TABLE 1. PERCENT OF AUDIT RESULTS WITHIN 1, 3, 5, 10, 15, AND 20 PERCENT OF THE ASSIGNED VALUE[a]

Audit	Level or plate no.	1%	3%	5%	10%	15%	20%
Carbon monoxide	1	20	48	79	94	97	99
	2	30	64	82	98	100	—
	3	23	72	89	98	99	--
Sulfate	1	16	37	56	75	80	85
	2	15	47	63	88	92	93
	3	12	42	67	82	91	95
Nitrate	1	15	46	57	75	84	91
	2	15	43	60	77	82	89
	3	20	46	63	83	89	94
Lead	1	13	47	65	83	90	94
	2	20	42	71	88	94	95
	3	21	44	74	90	95	96
Sulfur dioxide	1	10	30	48	82	95	97
	2	10	26	46	78	95	98
	3	6	20	42	70	88	94
Hi-Vol/ PM-10 (SSI)	5	3	23	34	62	74	82
	7	8	30	46	73	83	88
	10	18	44	60	81	89	91
	13	21	46	63	85	90	92
	18	21	47	64	86	92	93
	88	19	43	68	84	91	95

[a]AREAL's target criteria for acceptable performance of the audit is that the participant's value for each concentration/flow be within 15 percent of the assigned value (excluding the CO audit where the value is 10 percent). Participants reporting values outside these limits are urged to determine the cause for their poor performance and to take corrective action. Participants reporting results between 10 and 15 percent from the assigned value (5 and 10 percent for CO) are urged to try to reduce the size of the difference.

TABLE 2. AUDIT RESULTS FOR CARBON MONOXIDE

Level	n	Assigned value (ppm)	Mean (ppm)	% Diff.
		A. ALL DATA		
1	317	6.00	5.98	-0.33
2	315	14.50	14.77	1.86
3	315	36.00	36.65	1.81
		B. OUTLIERS REMOVED		
1	317	6.00	5.98	-0.33
2	314	14.50	14.75	1.72
3	313	36.00	36.71	1.97

TABLE 3. AUDIT RESULTS FOR SULFATE ON FILTER STRIPS

Audit	Level	n	Assigned value ($\mu g/m^3$)	Mean ($\mu g/m^3$)	% Diff.
			A. ALL DATA		
0288	1	39	4.00	4.16	4.00
	2	39	24.00	24.17	0.71
	3	39	9.80	10.04	2.45
0888	1	34	4.98	4.83	-3.01
	2	34	10.47	10.52	0.48
	3	34	21.42	20.63	-3.69
			B. OUTLIERS REMOVED		
0288	1	35	4.00	3.99	-0.25
	2	36	24.00	24.04	0.17
	3	38	9.80	9.89	0.92
0888	1	31	4.98	4.90	-1.61
	2	32	10.47	10.31	-1.53
	3	32	21.42	21.66	1.12

TABLE 4. AUDIT RESULTS FOR NITRATE ON FILTER STRIPS

Audit	Level	n	Assigned value ($\mu g/m^3$)	Mean ($\mu g/m^3$)	% Diff.
		A. ALL DATA			
0288	1	35	3.00	3.13	4.33
	2	35	5.50	5.46	-0.73
	3	35	10.00	9.77	-2.30
0888	1	30	13.01	12.86	-1.15
	2	30	5.02	5.07	1.00
	3	30	8.23	8.04	-2.31
		B. OUTLIERS REMOVED			
0288	1	30	3.00	2.97	-1.00
	2	32	5.50	5.58	1.45
	3	32	10.00	10.03	0.30
0888	1	30	13.01	12.86	-1.15
	2	28	5.02	4.95	-1.39
	3	30	8.23	8.04	-2.31

TABLE 5. AUDIT RESULTS FOR LEAD ON FILTER STRIPS

Audit	Level	n	Assigned value ($\mu g/m^3$)	Mean ($\mu g/m^3$)	% Diff.
		A. ALL DATA			
0188	1	71	0.58	0.57	-1.72
	3	71	1.48	1.69	14.19
	5	71	6.58	6.38	-3.04
0788	1	84	1.76	1.73	-1.70
	2	82	4.68	4.51	-3.63
	3	83	0.70	0.70	0.00
		B. OUTLIERS REMOVED			
0188	1	66	0.58	0.55	-5.17
	3	69	1.48	1.64	10.81
	5	69	6.58	6.52	-0.91
0788	1	82	1.76	1.75	-0.57
	2	80	4.68	4.59	-1.92
	3	81	0.70	0.71	1.43

TABLE 6. AUDIT RESULTS FOR SULFUR DIOXIDE CONTINUOUS MONITORS

Level	n	Assigned value (ppb)	Mean (ppb)	% Diff.
		A. ALL DATA		
1	247	406	391	-3.69
2	247	171	165	-3.51
3	247	50	48	-4.00
zero	96	0	2	NA
		B. OUTLIERS REMOVED		
1	243	406	391	-3.46
2	242	171	165	-3.51
3	238	50	49	-2.00
zero	96	0	2	NA

TABLE 7. AUDIT RESULTS FOR HIGH VOLUME/PM-10 (SSI) FLOW MEASUREMENTS

Plate number	n	Assigned flow (m^3/min)	Mean flow (m^3/min)	% Diff.
		A. ALL DATA		
5	463	0.76	1.24	63.2
7	589	0.91	1.24	36.3
10	639	1.11	1.51	36.0
13	655	1.23	1.62	31.7
18	675	1.35	1.69	25.2
88	443	1.14	1.24	8.8
		B. OUTLIERS REMOVED		
5	416	0.77	0.79	2.6
7	541	0.94	0.96	2.1
10	600	1.13	1.16	2.6
13	616	1.26	1.28	1.4
18	638	1.38	1.40	1.4
88	433	1.15	1.17	1.7

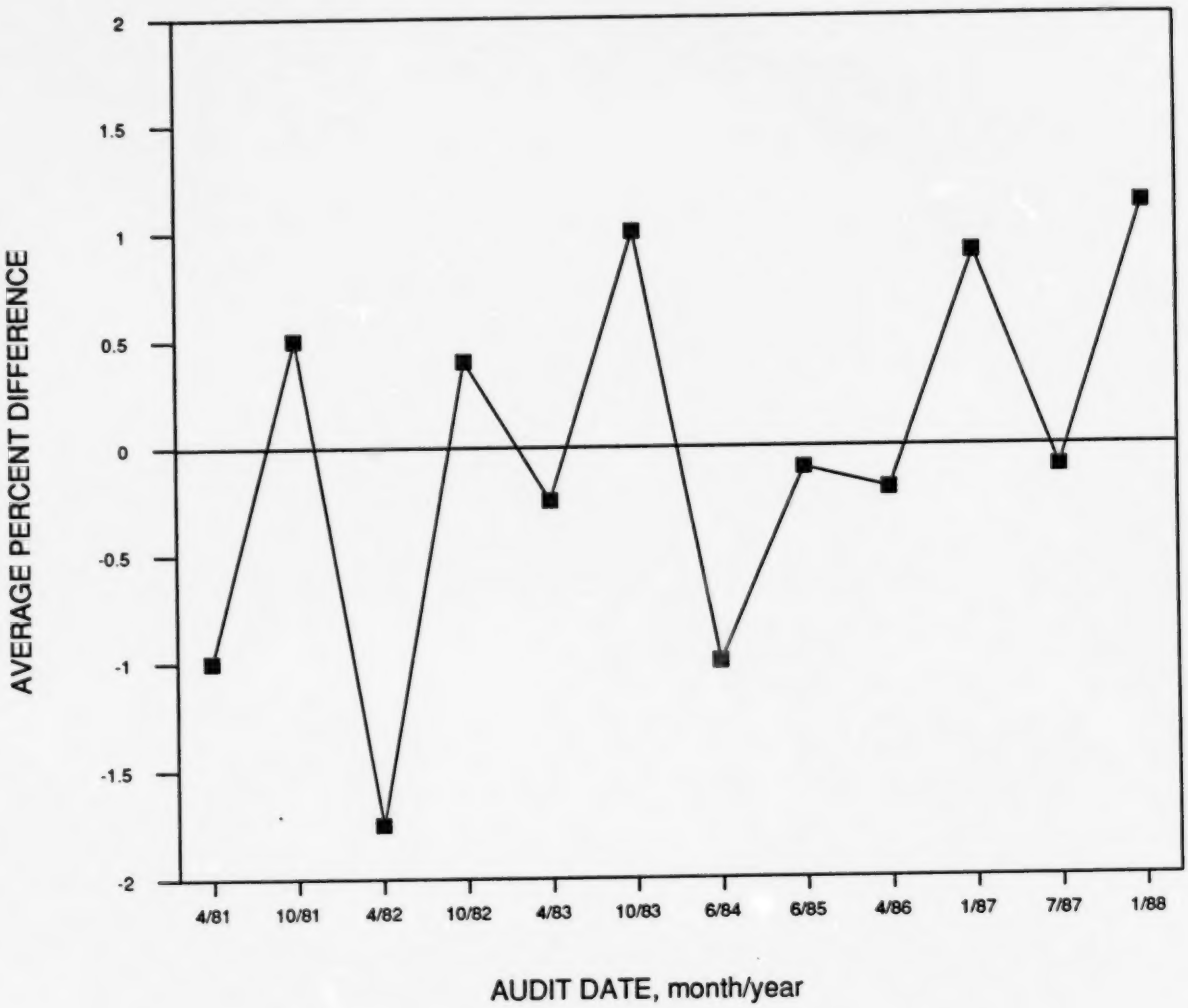

Figure 1. CARBON MONOXIDE AUDITS

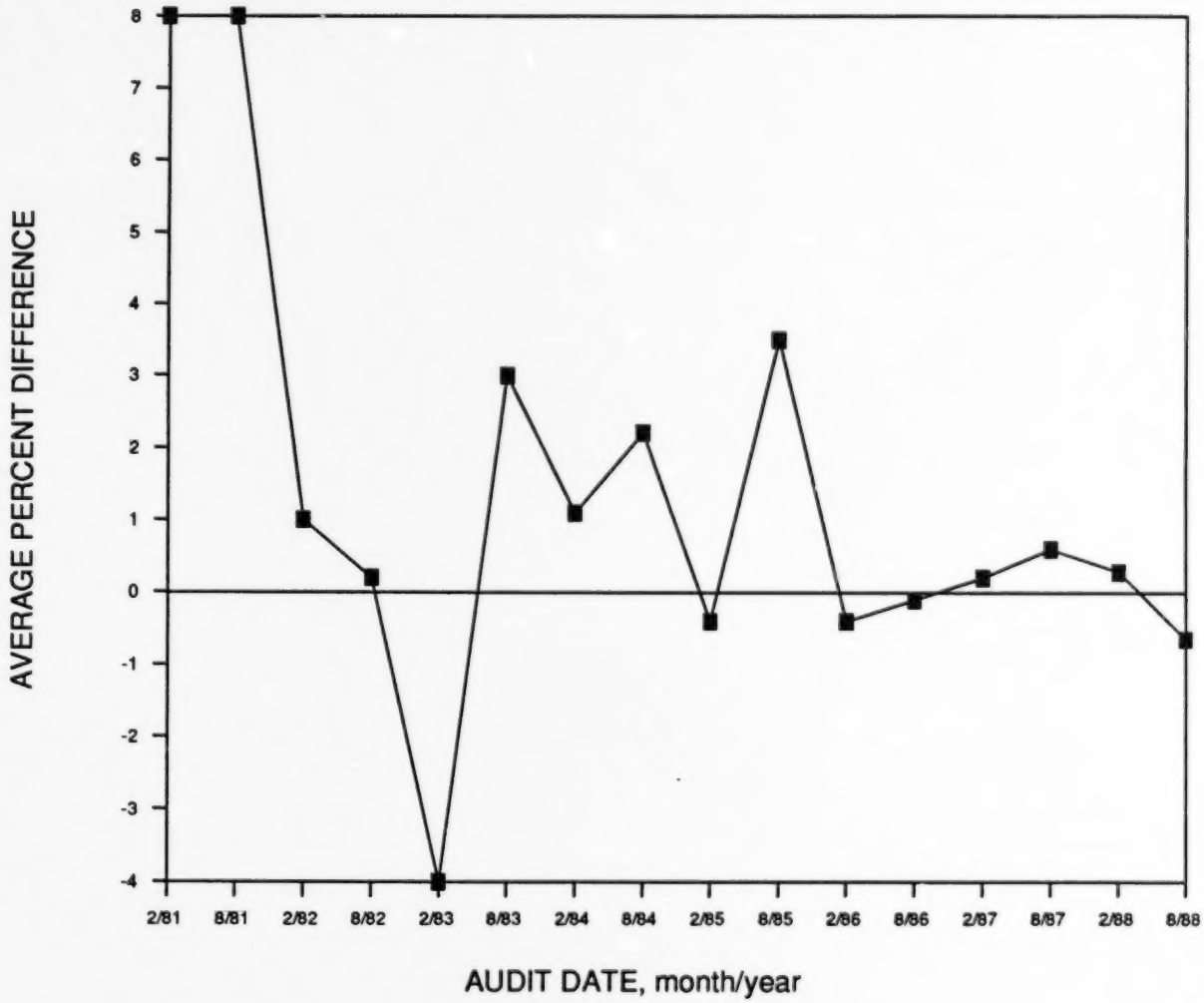

Figure 2. SULFATE AUDITS

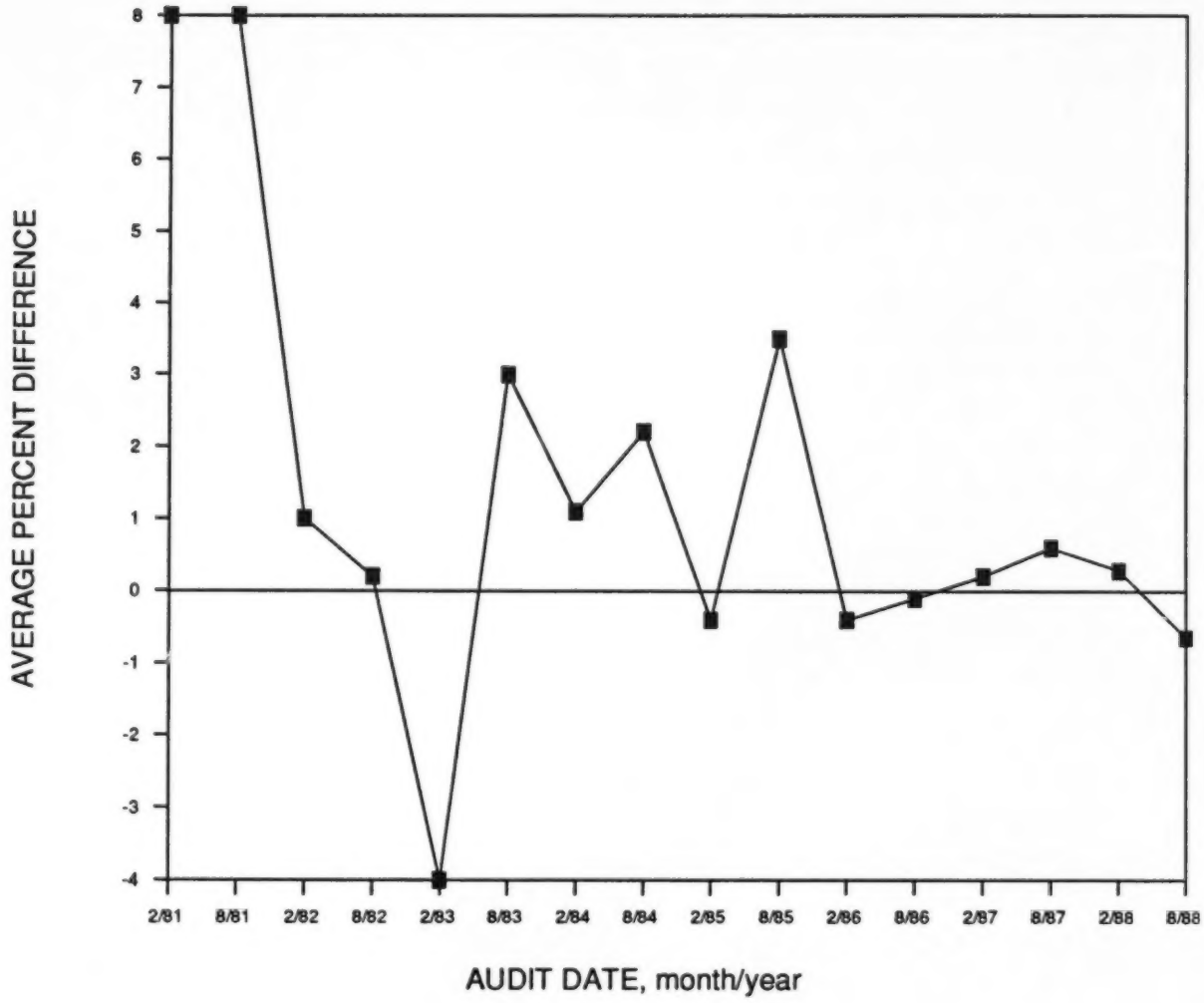

Figure 2. SULFATE AUDITS

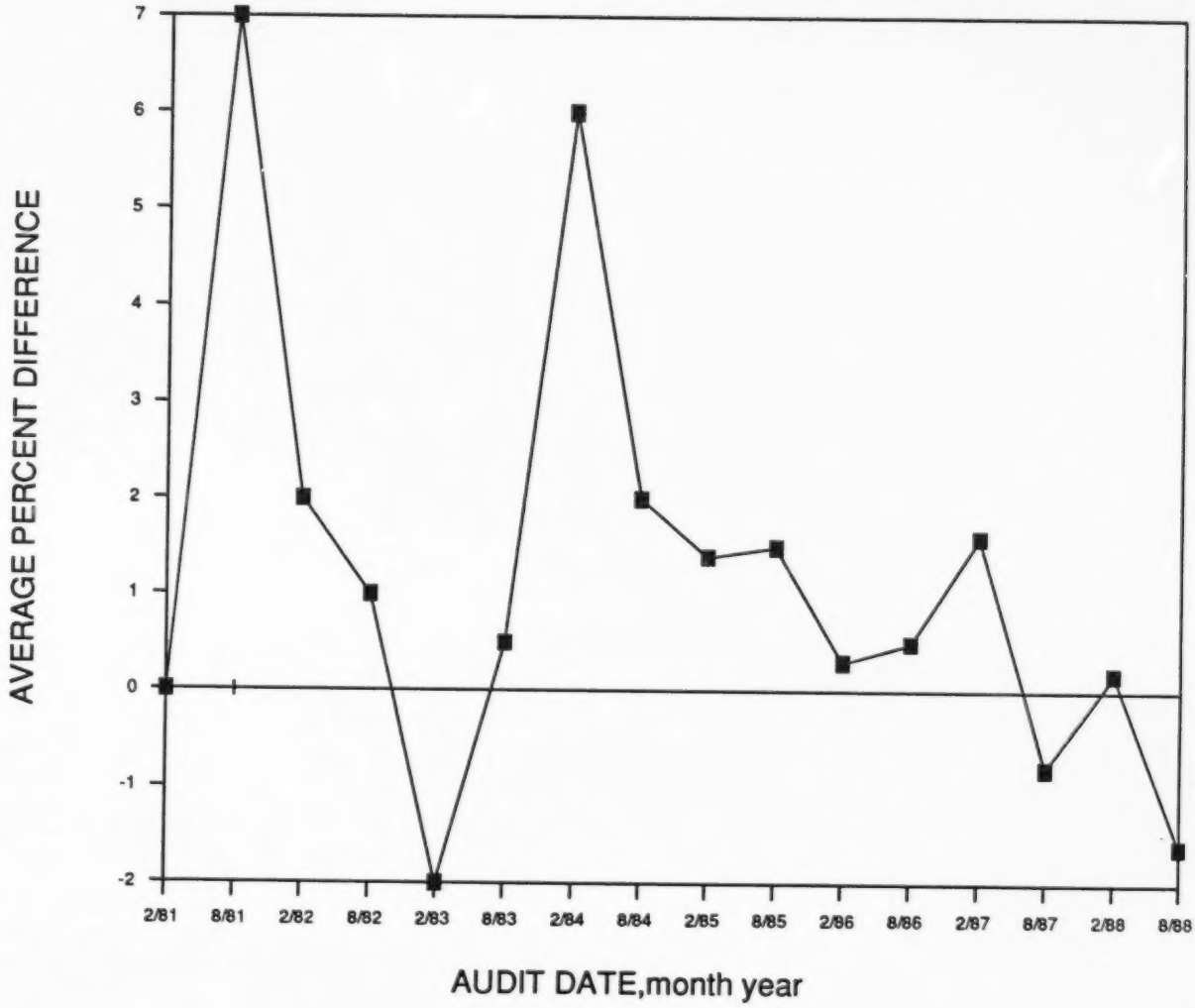

Figure 3. NITRATE AUDITS

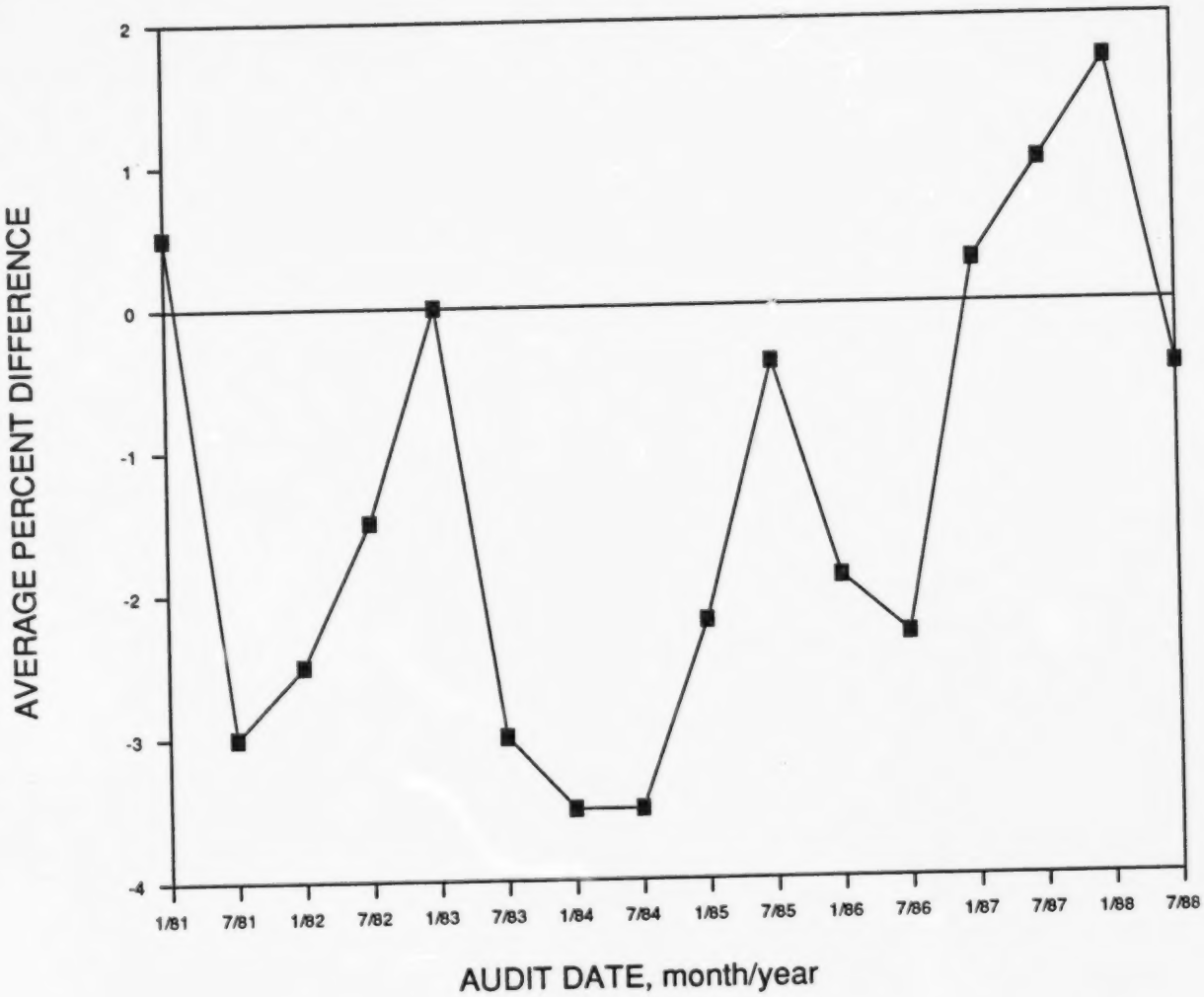

Figure 4. LEAD AUDITS